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XIII. On the constitution of the atmosphere. By John Dalton, Esq. F. R. S. &c. Communicated January 12, 1826.

Read February 24, 1826.

The fact discovered by Boyle and Marriotte, that the space occupied by air is in the inverse ratio of the pressure, is one of great importance in the doctrine of elastic fluids. It may probably not be mathematically true in extreme cases; but in those where the condensations and rarefactions do not exceed 50 or 100 times, there is reason to believe the above ratio is a very near approximation to the truth.

Sir Isaac Newton has shown in the 23d prop. book ii. of the Principia, that if homogeneous particles of matter were endued with a power of repulsion in the inverse ratio of their central distances, collectively they would form an elastic fluid agreeing with atmospheric air in its mechanical properties. He does not infer from this demonstration that elastic fluids must necessarily consist of such particles; and his argument requires that the repulsive power of each particle terminate, or very nearly so, in the adjacent particles. From the scholium to this proposition, Newton was evidently aware of the difficulty of conceiving how the repulsive action of such particles could terminate so abruptly as his supposition demands; but in order to show that such cases exist in nature, he finds a parallel one in magnetism.

Whatever we may think of the constitution of an elastic fluid, it is clear, that for the purpose of ascertaining its mecha-

nical effects, we may safely adopt the above hypothesis within the fore-mentioned limits of condensation and rarefaction.

The existence of elastic fluids totally different from atmospheric air in their chemical nature, but agreeing with it in mechanical properties, was unknown in Newton's time. Such fluids are now known to exist; they may be mixed together, and, in case no obvious chemical action ensues, they are found to occupy the same space after as before mixture, and in due time to be uniformly diffused through the space the mixture occupies, whatever may be the difference of their volumes and specific gravities: and such mixtures have all the mechanical properties of simple elastic fluids, as the atmosphere itself evinces, which is a mixture of at least four such elastic fluids.

Whether the uniform diffusion of elastic fluids through each other is occasioned by the repulsion of the elementary particles of the same kind, which appears to force them through most bodies, as well solid and liquid as aerial, except glass and the metals; or whether it is caused by attraction or chemical affinity, may be doubted. Difficulties attend both views. I have long been inclined to adopt the former notion as most consistent with the phenomena. According to this view the particles of any elastic fluid (A) are endued with repulsion to each other by the Newtonian law above stated; also those of any other (B) repel each other in like manner; but the particles of (A) do not repel those of (B), or rather are inelastic in regard to them. Such mixture must evidently possess the mechanical law of condensation which the atmosphere possesses, and which NEWTON's imaginary homogeneous fluid possesses.

All our ordinary experiments are limited to given volumes of gases which are considered of equal densities and temperatures throughout the volumes; but this is not the case when the volume is large, and extended in a direction perpendicular to the horizon; such, for instance, as a cylindrical column of the atmosphere of the altitude of several miles. The density in such vertical columns diminishes nearly in geometrical progression to equal intervals of ascent, and the temperature diminishes nearly in arithmetical progression, or in direct proportion to the ascent.

When we observe the diffusion of two gases (A) and (B) through each other in small limited volumes, such as in our ordinary experiments, we may ascribe it on the one hand to the mutual attraction of the particles of (A) and (B); or on the other, to the repulsion of the particles of (A) for each other, and their non-repulsion of those of (B); and vice versā. The effect would seem to be precisely the same on both views. But it is not so when we consider a vertical atmospherical column of mixed gases. Here the two views display their difference in a striking manner.

An exposition of the results of two indefinitely long perpendicular columns of any given gases (A) and (B) being mixed together, having never yet been laid before the philosophical public according to either opinion, I apprehend it may be of service to the advancement of knowledge on this interesting subject to draw attention to the following considerations.

Let A and B be two equal cylindrical tubes placed in contact and perpendicular to the horizon, of indefinite length, closed at the bottom and open at the top. Let the tube A have

an atmosphere of hydrogen gas in it, so as that it would support the mercury in the barometer at 30 inches. Let the tube B have an atmosphere of carbonic acid gas also capable of supporting 30 inches of mercury. Now supposing it possible for the atmosphere to be for a few moments of uniform density throughout the column, and that density the same as at the surface of the earth, the height of the hydrogen atmosphere would be about 66 miles, and that of the carbonic acid about 3.3 miles; or the heights would be in the ratio of 20 to 1 nearly. Afterwards, when the atmospheres were expanded to their natural extent, equal elasticities of the two gases would also be at altitudes as 20 to 1; that is, if at two miles of elevation the carbonic acid atmosphere supported 15 inches of mercury, that of hydrogen would support the same at 40 miles elevation. These are positions too obvious to be insisted upon. Conceiving now the atmospheres to have acquired their perfect equilibrium, or to be at rest in the respective columns, let numerous air-tight horizontal partitions be imagined across both tubes at equal intervals from the ground upwards. These intervals may be either small, as a foot, or larger, as a mile, as may suit our purpose.

Let now a communication be opened between each two horizontal portions of the tubes, either by a perforation or a small tube, as represented in the annexed figure, at 1, 2, 3, 4, &c. Then it is well known that the two gases would intermix, and finally obtain such equilibrium, that one half of the gas at first in each division would pass into the opposite division, and the other half remain where it was. Hence, the whole weight of gases in each whole tube would be still the

same as before, namely, 30 inches of mercury; half of which in each tube would be carbonic acid, and the other half hydrogen.

Very great differences would be found in the proportions of the two gases in ascending, viewing them either in regard In the lowest division, or No. 1, we to volume or to weight. should find equal volumes of carbonic acid and hydrogen. At the height of two miles, we should find about one volume of carbonic acid mixed with two of hydrogen; at the height of four miles, the carbonic acid would be to the hydrogen as one to four, nearly; and at the height of 40 miles, there would probably be no carbonic acid at all in either tube, but the hydrogen would there be of one half the density it was in Above this, or above the limits of the carbonic acid atmosphere, wherever it might be, there would be nothing but hydrogen gas in each tube up to the limits of the hydrogen atmosphere.

The limits of the atmosphere having been mentioned, it may be proper to observe, that on the hypothesis of the density of any atmosphere diminishing in geometrical progression to intervals of ascent in arithmetical progression, every atmosphere must be unlimited, or of infinite extent. But if any atmosphere is constituted of particles on the Newtonian hypothesis, it is obvious that such atmosphere must have a limit; this limit will exist where the repulsion of two particles becomes equal to the weight of one of them.

We have no data from which to determine the absolute height above the surface of the earth to which any one atmosphere can ascend; but we can form a pretty accurate comparison of the relative heights to which two atmospheres would ascend, especially if the relative weights of their atoms be known.

For instance; we know that the diameter of an elastic particle of carbonic acid is nearly, or exactly, the same as that of a particle of hydrogen under the same pressure; also that their weights are as 20 to 1. At two miles elevation, the elasticity of an atmosphere of carbonic acid gas is diminished one half; and at 40 miles elevation, that of hydrogen is diminished one half. Now let it be supposed that at 30 miles elevation the carbonic acid atmosphere ceases to exist, or terminates, at which elevation its elasticity must be according to the geometrical progression, nearly $\frac{1}{33000}$; then, by the same law, the elasticity of the hydrogen atmosphere must be $\frac{1}{33000}$ at the height of $15 \times 40 = 600$ miles; also the diameters of the particles of the two gases are still equal at those elevations, because they vary as the cube roots of the elasticities inversely; that is, if the diameters of the particles of carbonic acid and hydrogen at the surface of the earth be denoted by 1, that of carbonic acid at 30 miles will be represented by $\sqrt[3]{3000}$, and that of hydrogen at 600 miles elevation will also be $\sqrt[3]{3000}$. But by hypothesis, this distance is capable of supporting a weight as 20 (namely the weight of one atom of carbonic acid); the hydrogen atmosphere therefore must be further elevated till it is capable of supporting a weight only as 1 (namely, the weight of an atom of hydrogen); this will take place when the elasticity is still further diminished in the ratio of the cube of 20 to the cube of 1, or 8000 to 1. Hence, we shall have to extend the atmosphere about $13 \times 40 = 520$ miles further before it can terminate, or to the height of 1120 miles. In this estimate we have not

taken into consideration the variable force of gravity. At the height of 1400 miles the force of gravity is reduced one half, nearly; on this account the elevation of the hydrogen atmosphere will be increased between 1 and 2 hundred miles more, so as to make it amount to twelve or thirteen hundred miles. The variation of temperature in ascending does not materially affect our views.

Thus it appears that upon the assumption we have made, the hydrogen atmosphere must be 40 times the altitude of the carbonic acid atmosphere. If we had assumed the utmost height of the carbonic acid atmosphere less than 30 miles, the disproportion of the two heights would have been still greater; and if more than 30 miles, it would have been less; but in this case the absolute difference would be greater.

If it be true that atmospheres have limits, or certain degrees of rarefaction beyond which they cannot be extended, it will produce certain modifications in the mixtures of the two gases in our tubes A and B, which will now require consideration.

Suppose the cell 1000 to be that at the summit of the hydrogen column A, or where the hydrogen atmosphere terminated before any communication was made with the column B. Then, on opening the communication of that cell with the corresponding one of B, one half of the gass would flow out as usual; but the two cells, instead of being filled with the dilated gas, would only be half filled with it. The gas would fill the lower half of each cell, pressing upon the lower partition, and the upper half would exist as a void. The same remark would apply, but in a less degree, to the inferior cells 999, 998, &c. and it would not be till a descent

of 40 miles that the gas of one cell would be adequate to fill two cells, making the density in each the same as that in No. 1000 before the communication. In all that interval of 40 miles the continuity of the atmosphere would be interrupted, each cell having a partial void, and the partition having a pressure on it from above, and none beneath. In like manner it might be shown that the carbonic acid atmosphere, were it alone, and subsequently made to communicate with empty cells, would be two miles below the summit of the atmosphere before one cell of gas could fill two cells.*

After a complete equilibrium of intercourse had taken place between every two adjacent cells, let us next conceive all the horizontal partitions to be withdrawn from the two tubes, and consider what results will ensue.

It is evident the descent of the upper part of the hydrogen column in each tube would be immediate, as there would be vacuous places to fill up in it. The same would take place with the carbonic acid column; but the great body or weight of the mixed atmospheres would remain unchanged, except a slight condensation. The column of hydrogen in each tube would support 15 inches of mercury, and would in all respects resemble the upper half of the first column, A, of hydrogen gas, that supported 30 inches, excepting a slight difference occasioned by distance from the earth and temperature; and the same may be observed of the carbonic acid column in each tube. But would this constitution of the mixture be

^{*} Query, might not the absolute height of an atmosphere of carbonic acid gas (or any other) be found, by perfectly exhausting a tall receiver, then letting in a small given portion of the gas, and finding by some chemical test that the gas existed in the lower but not in the upper portion of the receiver?

permanent? Would a mixed atmosphere, which in fact as a whole, consisted of equal weights of carbonic acid and hydrogen, continue to exhibit at the surface of the earth equal volumes only in mixture? Or, on the other hand, would not the whole be wrought up in due time into one uniform composition in all its extent, of 20 volumes of hydrogen with one of carbonic acid, as many suppose to be the nature of the earth's atmosphere with regard to its component parts?

Before these questions are discussed we shall put the case in a different form: suppose a mixture of 20 volumes of hydrogen and one volume of carbonic acid (that is equal weights of each), were put into a large reservoir under the constant pressure of 30 inches of mercury, and from this reservoir were passed by means of a stop-cock into the indefinite perpendicular tube, A, perfectly void, till such time as the equilibrium between the reservoir and the tube was established: query, what would be the final arrangement of the two gases in the tube? I believe it will be allowed by all, that the final arrangement of the mixture of gases will be precisely the same in this case as in the one previously stated, whatever that arrangement may be.

Now I apprehend it is demonstrable, from what we know of the nature of mixed gases, that each of the two gases would be disposed just the same as if the other was not present. They would be mixed in equal volumes at the earth's surface; the carbonic acid would *rapidly* diminish in density in ascending, and terminate perhaps at 28 or 30 miles of elevation; the hydrogen would *slowly* diminish in density, and terminate perhaps at 11 or 12 hundred miles of elevation.

The arguments in support of this notion may be derived from the following facts:

1st. When two gases, not having a manifest chemical action upon each other, are put into a vessel of small limited capacity, they are found in a short time to be uniformly diffused through the capacity of the vessel, whatever be their proportions.

2d. Let a bottle, having its air exhausted, be half filled with water, and the other half with a mixture of equal volumes of two gases, suppose hydrogen and carbonic acid; then let an air-tight stopper be applied, and the contents of the bottle be duly agitated. The carbonic acid will be found equally diffused through the whole capacity of the bottle, the same in the water as out of it; but the hydrogen in the water will only be $\frac{1}{50}$ or $\frac{1}{60}$ of the density of that above the water. In this case each gas will be arranged, both within and without the water, precisely the same as if it was the only gas present. And if a third gas could afterwards be introduced into the bottle in like manner, it would take its place in and out of the water independently of the other two; and so on with any number. No pressure of any one gas on the surface of the water can confine another gas in the water; it must be a pressure arising from the same gas.

3d. If a portion of ether, alcohol, &c. be put into a bottle, and it be close corked, the vapour will ascend and fill the bottle, whatever air be present; its quantity and force will be the same whether there be any air, or none, being entirely regulated by the temperature.

From these three facts, but more especially from the two last, it appears to me as completely demonstrated as any

physical principle, that whenever two or more such gases or vapours as we have been describing are put together, either into a limited or unlimited space, they will finally be arranged each as if it occupied the whole space, and the others were not present; the nature of the fluids and gravitation being the only efficacious agents.

We may now apply this doctrine in considering the earth's atmosphere, on the supposition of its being in a quiescent state. The gases constituting it are azotic and oxygenous chiefly, a very small proportion of carbonic acid, and a small proportion of aqueous vapour. If we assume the weight of the atmosphere = 30 inches of mercury, and neglect the carbonic acid and aqueous vapour as inconsiderable in weight, we shall have $\frac{27}{100}$ of 30 = 6.3 inches for the weight of the oxygenous atmosphere, and $\frac{79}{100}$ of 30 = 23.7 inches for the weight of the azotic atmosphere. For the weights of the whole atmospheres on this view are proportional to the volumes found at the surface of the earth, and totally independent of their specific gravities. The weight of the aqueous vapour atmosphere is variable, and may be on an average = .4 of an inch of mercury, and that of carbonic acid = .03 of an inch of mercury.

The limit of altitude in a full atmosphere (of 30 inches mercury) of oxygen gas being assumed at 45 miles, that of an atmosphere of the same gas of 6.3 inches of mercury will be found by calculation on the above principles to be about 38 miles, the atom of oxygen being 7; and that of azotic gas of 23.7 inches weight will be found 54 miles, if the atom of azote be taken as 5; but if the atom of azote be double this weight, as is supposed by many, but I think without

sufficient reason, then the height of the azotic atmosphere will be only 44 miles. The very fine and attenuated carbonic acid atmosphere must ascend to the height of 10 miles, if a full atmosphere of this gas ascend to 30 miles; and that of steam or aqueous vapour to the height of 50 miles, allowing the specific gravity of steam to be .625, and the weight of its atom to be 8.

It may be worth while to contrast this view of the constitution of the atmosphere with the only other one, as far as I know, that has been entertained.

According to one view.

1. The volumes of each gas found at the surface of the earth are proportional to the whole weights of the respective atmospheres.

Weight of atmosphere.

Azote
$$-\frac{79}{100} = 79$$

Oxygen $-\frac{21}{100} = 21$

Aqueous vap. $=\frac{1}{75} = 1.33$

Carbonic acid $=\frac{1}{1000} = .10$

According to the other view.

1. The volume of each gas found at the surface of the earth multiplied by its specific gravity, is proportional to the whole weight of the respective atmosphere.

Sp. gr. Weight of atmosphere.

Azote
$$-\frac{79}{100} \times .97 = 76.6$$

Oxygen $=\frac{21}{100} \times 1.11 = 23.3$

Aque. va. $=\frac{1}{75} \times .625 = 0.83$

Car. acid $=\frac{1}{1000} \times 1.53 = 0.15$
 $=\frac{1}{100.88}$

^{*} In order to show the ratios more completely we have assumed the two compound atmospheres differing a little in the total weights.

According to one view.

- 2. The altitude of each atmosphere differs from that of every other, and the proportions of each in the compound atmosphere gradually vary in the ascent.
- 3. When two atmospheres are mixed, they take their places according to their specific gravity, not in separate strata, but intermixedly. There is however a separate stratum of the specifically lighter atmosphere at the summit over the other.

According to the other view.

- 2. The altitude of each atmosphere is the same, and the proportion of each in the compound atmosphere is the same at all elevations.
- 3. When two atmospheres are mixed, they continue so, without the heavier manifesting any disposition to separate and descend from the lighter.

All that we have said hitherto has been relating to quiescent atmospheres, or such as are in a state of perfect equilibrium. How the case would be with regard to the earth's atmosphere, such as it actually is, in a state of continual motion and agitation greater or less in all its parts, it is not very easy to ascertain; and it is besides rather a question to be decided by experiment and observation than by any theory. I have a series of observations made on this subject; but as they will require to be submitted in a considerable detail, I shall reserve them as a sequel to this essay on some future occasion.



From the Press of W. NICOL, Cleveland-row, St, James's.